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# Composition & Analysis Of Portland Cement

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# The Composition and Analysis of Portland Cement

BY

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## THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

William J. Donoghue

ENTITLED The Composition and Analysis of Portland Cement

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Arts

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# PORTLAND CEMENT.

## Its Chemical Composition, and Analyses of Some Cements.

Definition.--Portland cement is a product resulting from the heating to incipient fusion of a mechanical mixture of limestone and clay, or similar materials containing silica, lime and alumina, and then grinding finely the resulting clinker[7]. When the fine powder is mixed with water, chemical action takes place and a hard mass is formed. The change undergone by the cement mortar in passing from the plastic to the solid state is termed "setting". This usually requires but a few hours at most. On completion of the set a gradual increase in cohesive strength is experienced by the mass for some time, and the cement is said to "harden". Cements usually require from six months to a year to gain their full strength. Cement differs from lime in that it hardens while wet and does not depend upon the carbon dioxide of the air for its hardening. It is very insoluble in water and is adapted to use in moist places or under water where lime mortar would be useless[8].

Composition of Cement.--According to Le Chatelier's theory[2], Portland Cement consists of a mixture of tri-calcium silicate.

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[7]--German standard rules. [8]--Examination of Portland Cement.--Meade. [2]--Comptes Rendus, Vol. 94, page 867. Annals des Mines, 1887, page 345.

$3\ CaO.\ SiO_2$, and tricalcium aluminate, $3\ CaO.\ Al_2O_3$. Le Chatelier made this conclusion after a long series of experiments, these consisted in examining thin sections of cement clinker under the polarizing microscope. He also made many experiments upon the synthetic production of calcium silicates and aluminates by heating intimate mixtures of finely pulverized silica, alumina, and lime. He then studied the hydraulic power of the compound thus prepared. He did not succeed in preparing the tricalcium silicate directly by heating lime and silica the result of the attempt being a mixture of lower silicates and lime. He gave it as his opinion that this compound could be prepared indirectly by heating together a mixture of fusible silicates and lime. The tricalcium silicate is the essential element of Portland Cement. In this compound the lime and silica bear the ratio of 2.78 to 1.

Assuming that in tricalcium silicate three molecules of lime (Ca O) are united to one of silica, that in tricalcium aluminate three molecules of lime are united to one of alumina, and that these two compounds are the essential constituents of Portland Cement, Le Chatelier gives the following as the ratio between the lime and magnesia--the basic elements and the silica and alumina the acid elements in a good cement--

$$\frac{CaO\ MgO}{SiO_2\ Al_2O_3} \overset{<}{=} 3 \qquad (1)$$

and $$\frac{CaO\ MgO}{SiO_2-Al_2O_3-Fe_2O_3} \overset{>}{=} 3 \qquad (2)$$

LeChatelier says that (1) usually gives for a good cement 2.5 to 2.7 and (2) from 3.5 to 4.

The ratio between the silica and alumina on the one hand and the lime on the other is termed "Hydraulic index".

Messrs. Spencer. B. and W. B. Newberry[3], after a long series of researches on the constitution of Portland Cement, arrived at conclusions somewhat different to those of Le Chatelier. They prepared silicates and aluminates of lime synthetically by heating together in a Fletcher gas furnace intimate mixtures of finely pulverized quartz and calcium carbonate and alumina and calcium carbonate in different molecular proportions.

They examined the hardening and setting properties of the resulting compounds. These chemists agreed with Le Chatelier that the silica in Portland Cement is present as tricalcium silicate, and that to this is due the ultimate hardening of cement, they had no difficulty in preparing the tricalcium silicate directly, by heating together silica and lime in the molecular proportion of 1 to 3. The experiments led Messrs. Newberry to conclude that the alumina is in combination with the lime as dicalcium aluminate and not as tricalcium aluminate. The conclusions from their experiments are as follows:

"First".--Lime may be combined with silica in the proportion of 3 molecules to 1, and still give a product of practically constant volume and good hardening properties, though hardening very slowly. With 3 1/2 molecules of lime to 1 of silica the product is not sound, and cracks in water.

"Second".--Lime may be combined with alumina in the proportion of 2 molecules to 1, giving a product which sets quickly,

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[3] --J. Soc Chen Ind., 11, 1035.)

but shows constant volume and good hardening properties. With 2 1/2 molecules of lime to 1 of alumina the product is not sound".

The Newberry Formula.--The formula for the tricalcium silicate, $3\,CaO, SiO_2$, corresponds to 2.8 parts by weight of lime to 1 part of silica, and the formula for the dicalcium aluminate, $2\,CaO, Al_2O_3$, corresponds to 1.1 parts of lime to 1 of alumina. From this the following formula is given as representing the maximum of lime which should be present in a correctly balanced Portland Cement: per cent lime = per cent silica $\times$ 2.8 + per cent alumina $\times$ 1.1.

They found that cement prepared synthetically with lime, alumina, and silica proportioned according to the above formula gave good results, whereas that prepared by Le Chatelier's formula was unsound, showing the lime to be in excess.

Substances Found in Cement.--From this it will be seen that the essential ingredients of Portland Cement are lime, silica, and alumina. A little of the alumina is always replaced by ferric oxid , and some of the lime by magnesia. Small percentages of alkalies, potash and soda, present in the clay as silicates, are also in cement, while the most thorough burning fails to drive off all the carbon dioxide from the limestone or marl in the raw mixture, leaving traces in the finished product. Coal contains sulphur; this when burned becomes sulphur dioxide, a gas which is absorbed by the uncombined lime of the cement mixture forming calcium sulphate. These are the chemical constituents for which cements are mainly analyzed.

## Analysis of Various Portland Cements.

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $CaO$ | $MgO$ | $K_2O$<br>$Na_2O$ | $SO_3$ | $CO_2$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| English Portland | 23.31 | 5.85 | 4.65 | 60.90 | 0.90 | 0.30 | 2.43 | | 1.40 |
| " " | 22.04 | 7.35 | 4.14 | 61.94 | 0.91 | 0.59 | 1.38 | | 1.65 |
| " " | 19.55 | 10.65 | 3.30 | 59.55 | 2.41 | 0.88 | 2.08 | | 1.40 |
| " " | 27.74 | 7.74 | 3.70 | 56.68 | 0.57 | 0.63 | 1.66 | | 6.28 |
| Belgian Portland | 27.18 | 8.85 | | 59.50 | 1.41 | | 0.99 | | |
| " " | 25.60 | 6.13 | 3.47 | 60.19 | 0.70 | | 1.13 | | 2.70 |
| French Portland | 22.20 | 6.72 | 2.28 | 67.31 | 0.95 | | 0.26 | | 0.40 |
| " " | 26.00 | 6.65 | 2.75 | 61.60 | 1.08 | | 0.84 | | 1.10 |
| German Portland | 22.63 | 7.06 | 2.42 | 60.81 | 2.89 | 2.83 | 0.47 | 0.33 | |
| " " | 22.85 | 5.51 | 2.76 | 65.59 | 1.24 | 0.92 | 1.69 | | |
| American Portland | 20.80 | 7.39 | 2.61 | 64.00 | | | | | |
| " " | 23.48 | 9.42 | | 62.90 | 1.20 | 0.90 | 1.25 | | trace |
| " " | 22.89 | 8.00 | 2.44 | 63.38 | 2.30 | | | | 0.99 |
| " " | 22.89 | 8.00 | 2.44 | 63.38 | 2.30 | | | | 0.99 |

Lime.--A good cement contains from 58 to 67% lime, the amount depending upon the relative proportion of silica and alumina, and also upon the care with which the cement has been manufactured. Up to the limit it may be said that the more lime that is present in a cement the greater will be its strength. The limit is reached, however, when more lime is present than will combine chemically with the silica and alumina, leaving some lime in the uncombined state, or, as Newberry's formula puts it, when the percentage of lime is greater than the percentage of silica multiplied by 2.8 plus the percentage

of alumina miltiplied by 1.1. Lime in slaking expands so that an excess of lime over what will unite with the silica and alumina will cause the cement to expand and crack. If the lime is much under the limit, the cement will contain clay in excess for the lime will not be present in sufficient quantity to change all the clay to silicates and aluminates. This excess of clay, of course, is devoid of cementing qualities and may be looked upon as just so much foreign matter. Though it will not cause the cement to fall to pieces subsequently, it takes away from its strength because in its place should be cement. The amount of lime a cement will bear depends upon the care with which the mixture of raw materials is made. Thus poorly ground, imperfectly mixed raw materials would probably result in a very much over-limed cement, if the lime limit ( as shown by chemical analysis of the clay, marl, limestone or cement rock of the mixture) was anywhere near reached, for the coarse particles of calcium carbonate would not come into sufficient close contact with the silica and alumina to completely combine with the latter. A properly burned cement will also stand a greater percentage of lime than an improperly burned one. A cement in which the temperature at burning was too low to heat all the lime to the point of combination with the silica and alumina, would naturally contain free lime. Chemical analysis, therefore, if taken alone as the guide to a cement, will seldom tell us much, where the lime content is concerned; as of two cements containing the same quantity of lime, one properly made might be quite sound, while the other, from faulty mixing and burning, might be anything but sound. A method of determining the uncombined lime in cement would enable us to tell whether agiven cement is sound or not, but unfortunately no method of accurately

determining this constituent is now known, so that the physical tests must be resorted to as a test of Cement.

## History.[6]

The deep debt which we owe to Portland cement is hardly recognized as widely as it should be. Its invention alone rendered possible many of the extraordinary architectural, and more especially engineering feats of the past century, and when properly prepared, its durability far exceeds that of many bricks and building stones. Its present excellence is the outcome of years of patient scientific investigation and, although the names of its inventors and perfectors (who labored principally during the first half of the nineteenth century) are forgotten, or at best but dimly remembered, the result of their work has revolutionized and assisted design to as great, or, perhaps, greater an extent than has the introduction of mild steel for construction purposes.

Smeaton's research work.--Whilst he was building the Eddystone Lighthouse, he became convinced that the theories of the ancients were incorrect and that lime burnt from hard stone did not of necessity give the hardest mortar. He noted also the important fact that many impure limes which contained a fair amount of clay made an excellent hydraulic cement. Prior to his day it had not been generally recognized that it was an advantage to calcine clay and lime together, and so benefit from the partial chemical combination

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[6] --Redgrave's, Calcareous Cements.

effected. Smeaton, however, did not turn his knowledge to financial account, and it remained for James Parker, (Parker's patent provided for the preparation of cement from septaria or nodules present in clay.) of Christ Church, in the County of Surrey, to invent and patent a cement in 1796, to which some years afterward he applied the unfortunate misnomer of "Roman", giving rise to the theory that this material was originally prepared by the invaders of Britain. The deposits from which Roman cement was made varied widely in their composition, the resultant cements differing considerably. After the lapse of a few years, Parker began to prepare his material from pebbles found on the Isle of Sheppy, Whitstable, and Harwich. At the same time the name was altered to "Parker's Cement", which was the immediate **precursor** of the material now so well known.

In the year 1813 Joseph Aspdin, a Leeds bricklayer, succeeded in manufacturing cement from lime-stone, which had been reduced to powder, and clay. He patented this in 1824, and called the substance "Portland Cement" because of its fancied resemblance to Portland stone.

Aspdin's specification, No. 5,022, is dated October 21, 1824, and is for "An Improvement in the Modes of Producing Artificial Stone", which invention he thus describes: "My method of making a cement or artificial stone for stuccoing buildings, water works, cisterns, or any other purpose to which it may be applicable ( and which I call Portland Cement), is as follows: I take a specific quantity of limestone, such as that generally used for making or repairing roads, after it is reduced to a powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself and I cause the powder, or limestone, as the

case may be, to be calcined. I then take a specific quantity of argilloceous earth or clay and mix them with water to a state approaching impalpability, either by manual labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation. Then I break the said mixture into suitable lumps and calcine them in a furnace similar to a limekiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into the consistency of mortar and thus applied to the purposes wanted.

In the year 1825 Aspdin established a manufactory at Wakefield for his cement, and in 1828 Sir More Isambard Brunel and his son, Mr. Isambard Kingdom Brunel, are said to have used this material on the Thames Tunnel. Aspdin's cement, after it had been fired, was only in a semi-burnt condition, proper vitrification had not taken place, or, if it had taken place, those portions of clinker which approximated to blackness were thrown aside and considered inert, whereas in reality the best material was rejected.

It was General Pasley who, at a later date, discovered first the value of burning lime and clay to a joint of incipient vitrification. James Proat, builder, of Finchley, should also be mentioned as one of the pioneers of the industry, as he in 1825 established himself in cement works at Swanscombe, the site, being the same as that now used by Messrs. Bazley, White and Co. In the year 1830 General Pasley, then Inspector of the Royal Engineers' School at Chatham, independently produced a fair hydraulic cement from the

Medway clay and chalk, and he appears to have continued his researches for some time. He mentioned, in the second edition of his book on the subject (1847) that there were three manufacturers of artificial cements in England who turned out satisfactory materials--Messrs. J. B. White, Swanscombe, Kent (who had taken over Frost's works at that date), Messrs. Evans and Nicholson, of Manchester, who were manufacturing what they called a patent lithic cement, and Richard Graves, of Stratford-on-Avon, who was preparing blue lias cement. It is fairly certain, however, that General Pasley underestimated the number of manufacturers, Aspdin's Wakefield factory being among those omitted.

In the year 1843 Messrs. Grissel and Peto, contractors for the House of Parliament, conducted a series of comparative tests between Roman and Portland cements, consisting of the breaking weights borne by brick beams and cantilevers. Their letter to the manufacturer states that they were satisfied that a mortar composed of three parts sand to one part Portland cement was more than double the strength of the Roman mortar, although the latter had only one part sand. Messrs. Grisel and Peto's experiments advertised the material, and as they used it extensively on the numberless and extensive works of an architectual and engineering nature upon which they were engaged, the demand steadily rose. In the years of the railway mania, 1846-50, prices ran up for all hydraulic cements, so much so, in fact, that Sir Robert Peel, fearing exhaustion of septaria, proposed putting a tax upon it; but Mr. Aspdin interviewed Sir Robert, assuring him that even if the supply of Harwich stones failed (from which the Roman cement was manufactured), there was a

better material on the market, and one which was inexhaustible.

Experiments as to the crushing weights which could be borne by the two rival materials were conducted at Messrs. Bramah's works in 1848, and reported in the Builder of September 30th. of that year, the results showing most conclusively the superiority of Portland Cement.

In the year of the Great Exhibition (1851), experiments for tensile strength were made at the building, and this is the more interesting because it was here that briquettes first appeared. In 1859 the main drainage of London was about to be carried out, and the Board of Works were fortunate in selecting as their engineer Mr. J. Grant, M. Just C. E., who was the first to take testing in hand in a systematic and scientific manner. His researches were brought before the Institution of Civil Engineers, and attracted so much notice that Roman cement soon became little more than a memory. The discussion on Mr. Grant's various papers not only had the effect of further popularizing Portland Cement, but immediately improved its manufacture, owing to the free interchange of thought between engineers and manufacturers.

## Manufacture.[6]

The present day, Portland cements vary considerably from those prepared underAspdin's specification, which neither provided for a definite proportion between the limestone and argilloceous matter, nor for burning of the mechanical mixture to a condition in which true chemical combination had taken place. It is in the care-

ful observance of these two points, however, that one of the principal secrets of excellence in our present cements is found.

There are four principal methods of manufacture, viz:--

1. Wet process.
2. Semi-dry or Goreham process.
3. Dry process.
4. Rotary process.

(1) In the wet process, which is in vogue at some of the Thames and Medway works, chalk and clay are mixed together in definite proportions in a wash-mill and with an excess of water. The mill consists of a round pit in which there are horizontal revolving arms fitted with vertical "tynes" or teeth, by which the chalk and the clay are broken up and their particles reduced to a fine state of division. The resultant mixture, called slip or slurry, is then elevated to settling reservoirs, where the supernatant water is drawn off, or to drying chambers on top of the kilns, where waste gases from the flues absorb the excess of water. When the slip has been partially dried, it is chopped out in rough blocks, laid in kilns with layers of coke, the latter material being in the proportion of 8 or 9 cwt. to every ton of clinker produced[1]. The amount of fire required depends very largely, of course, on the quantity of moisture retained in the slip when kilned. There are almost numberless, and most ingenious varieties of kilns, having for their object the utilization of as great a proportion as possible of the waste gases from

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[1]--One ton of clinker roughly=1 1/2 tons of dry, raw materials, which will be in the approximate ratio of 1 1/8 tons of chalk to 3/8 ton of clay)

the burning of the clinker.

The changes effected in the kilns are various, but the main alteration is due to the liberation of the carbonic dioxide from the lime by the intense heat. The lime, deprived of this gas, is in such a condition that it will readily enter into chemical combination with the silica and alumina of the clay, forming silicates and aluminates of lime; it is upon the correct formation of these chemical compounds that subsequent success of a cement depends. When the kiln charge has been burnt through, it is drawn, and (in the better class works) the unburnt portions of the slip are picked out by hand for recalcination. The properly formed clinker, which is almost black, but not glossy in appearance, is taken away to crushers, where it is reduced in size prior to being passed through the x grinding mills. As in the case of the kilns, there is a very great variety in the design of these mills, but the mechanical details hardly appear to come within the scope of this thesis. The final grinding of the cement should reduce the clinker to an exceedingly fine, almost impalpable flour, as, other things being equal, the commercial value of a cement will be in inverse proportion to the size of its grain. This point however, I will take up later. After leaving the mill, the finished cement passes along a shoot or trough to the store, where it lies more or less exposed to the air until it is bagged up for delivery.

(2). The Goreham or Semi-Dry Process is one in which only about one quarter of the water required in the wet process is used in the wash-mill, but the mixture is further incorporated by passing the resultant slip between horizontal millstones or edge-runners. In my opinion, this system is vastly superior to the wet process, as

(taking one point only) the heat required to develop power to work the millstones is nothing like so great as that required to reduce the excessive moisture in the slip prepared by the wet process. The subsequent grinding, etc., of the cement is practically the same as that already described under heading 1.

(3). The Dry Process is used in some parts of Wales and in Warwickshire, where the interstratified limestone and sholes of lias formation supply the materials for making cement. The raw materials are mixed in proportions varying according to their chemical composition, they are then crushed, ground to powder, mixed with water, and passed through a pair of wet stones, which incorporate the mixture as in the case of the Goreham Process. They are then dried, loaded into kilns, burnt, and ground.

(4). The Rotary Process of preparing cement is largely used in the United States. In the first three processes described there are at least two serious drawbacks, due to waste of heat and to imperfect burning. The rotary process of manufacture was invented by Mr. F. Ransome of England, and carried a stage further towards perfection by Mr. Wilfred Strokes. A difficulty, however, was met with which at the time seemed insurmountable, but the ingenuity of the Americans has overcome this obstacle, and now the process is a commercial success. Theprocess consists in burning the slip in a slightly inclined revolving cylinder, the feed being at the far end from the burner, which is supplied with injected coal dust fuel. The material slowly finds its way down the cylinder, and, at a distance of approximately 10 ft. from the burner, the snitering begins. When the clinker drops from the first cylinder where it heats the air passing to the coal dust burner. After leaving the second cylinder

the clinker passes through crushing rolls (which are sprayed with water) which reduce the coarser lumps before the material passes into the third cylinder, where it is further cooled and pulverized prior to dropping into the trucks which take it to the grinding-mill. It is stated that the damping in the rolls has a beneficial effect upon the resultant cement, and that the material prepared by this process requires little subsequent aeration. The cost of production is said to be approximately three-fourths of that of the cheapest process (any of the other processes).

## Use.

With a full realization of its value, the present-day builders have used cement for a larger variety of purposes and for operations of greater importance than ever before attempted. One has but to recall the numerous instances of its success to realize how great a victory cement construction has attained over natural stone. Bridges, foundations, docks, buildings, floors, canals, dams, reservoirs, sidewalks, roadways, and building blocks represent a few of the important works constructed entirely of cement concrete. They mark but the beginning of the use of cement in the field of engineering and architecture; the future will witness even a fuller appreciation of its merits and a still wider field of usefulness.

# OUTLINE OF EXPERIMENTS.

While Portland cements have been carefully studied by many chemists, however, the subject is not exhausted, as there are still many points in question. Of these the following may be mentioned; first, what is the complete action of water on cement; secondly, the detection of adulteration; thirdly, is free lime present in cement; fourthly, rapid methods of analysis, and fifthly, the theories set forth for the constitution of Portland Cement donot entirely agree.

I conducted my work along the following lines. (1) Attempt to find out whether the alkalimetry test on the water extract of Portland cement was a means of determining free lime (CaO) or to see if a test of this kind afforded a chemical test for cements. (2) Study of water extract to see if it contains all the $SO_3$ that the cement contains. (3) Study of the water extract of cement after a definite length of time as on ten minutes contact with water. (4) The study of the action of ammonia chloride on distillation, with cement in the presence of water.

The work in detail is as follows:--(1) Attempt to find out whether the alkalimetry test of the water extract of the Portland cement was a means of determining free lime, or to see if a test of this kind afforded a chemical test for cements.

With this end in view I took 10.0 grams of Portland cement

(of various brands) and treated it with a thousand c.c. of freshly boiled water. I let this stand one day and on the following day I titrated 100 c.c. from each with N/10 HCl. Then on the same day I diluted 500 c.c. of the water extract, together with the cement residue to 1000 c.c. The next day, or on one of the following days, I titrated 100 c.c.of the water extract, as previously stated.

Results:-

Used Sandusky--Dycherhoff--Alsen Brands of Cement.

First Day.

Treated 10 grams of cement with 1000 c.c. of water.

Second Day.

| | | Alkalimetry. |
|---|---|---|
| Sandusky | 100 c.c. Water Extract | 15.4 c.c. N/10 HCl. |
| Dycherhoff | " " " " | 10.5 c.c. " " |
| Alsen | " " " " | 16.6 c.c. " " |
| Second Day.<br>500 c.c. water extract plus Cement Residue<br>diluted to 1000 c.c. | | |
| Third Day. | | |
| Sandusky | 100 c.c. Water Extract | 11.8 c.c. N/10 HCl |
| Fifth Day. | | |
| Dycherhoff | 100 c.c. Water Extract | 14.1 c.c. N/10 HCl |
| Alsen | " " " " | 21.95 c.c. " " |

Now I took .5 grams, 1.0 grams, 2.0 grams, 3.0 grams, 4.0 grams and 5.0 grams of Sandusky Portland Cement and treated each as I did the 10 grams, i.e., with 1000 c.c. freshly boiled water and conducted the work similarly to when I used the 10 grams cement.

Results:--

First Day.

Treated .5, 1.0, 2.0, 3.0, 4.0,&5.0 gr. with 1000c.c. water.

Fourth Day.

| | | | | | | Alkalimetry. | | |
|---|---|---|---|---|---|---|---|---|
| .5 gr. | Sandusky,-- | --100 | c.c. | Water | Extract | 4.3 c.c. | N/10 | HCl |
| 1.0 gr. | " | " | " | " | " | 6.0 c.c. | " | " |
| 2.0 gr. | " | " | " | " | " | 9.35 c.c. | " | " |
| 3.0 gr. | " | " | " | " | " | 13.8 c.c. | " | " |
| 4.0 gr | " | " | " | " | " | 14.3 c.c. | " | " |
| 5.0 gr. | " | " | " | " | " | 15.4 c.c. | " | " |

Fourth Day.

500 c.c. of each of the water extracts plus the cement residues diluted to 1000 c.c.

Fifth Day.

| | | | | | | Alkalimetry. | | |
|---|---|---|---|---|---|---|---|---|
| .5 gr. | Sandusky-- | -100 | c.c. | Water | Extract | 2.55 c.c. | N/10 | HCl |
| 1.0 gr. | " | " | " | " | " | 3.6 c.c. | " | " |
| 2.0 gr. | " | " | " | " | " | 5.4 c.c. | " | " |
| 3.0 gr. | " | " | " | " | " | 8.75 c.c. | " | " |
| 4.0 gr. | " | " | " | " | " | 9.5 c.c. | " | " |
| 5.0 gr. | " | " | " | " | " | 12.3 c.c. | " | " |

Now I took .5 and 1.0 gram of Sandusky cement treated each with 1000 c.c. of water and made the alkalimetry of 100 c.c. of the water extract every hour.

Results:--

During first hour.

Treated .5 and 1.0 gram Sandusky cement with 1000 c.c. of water and titrated 100 c.c. water extract as follows:-

| | Alkalimetry. |
|---|---|
| End of first hour, 0.5 gr. Sandusky | 1.3 c.c. N/10 HCl |
| 1.0 gr. " | 3.5 c.c. " " |
| End of second hour, 0.5 gr. Sandusky | 1.85 c.c. N/10 HCl |
| 1.0 gr " | 4.55 c.c. " " |
| End of third hour, 0.5 gr. Sandusky | 1.85 c.c. N/10 HCl |
| 1.0 gr. " | 5.15 c.c. " " |
| End of fourth hour, 0.5 gr. Sandusky | 4.55 c.c. N/10 HCl |
| 1.0 gr. " | 5.1 c.c. " " |
| Next Day, 0.5 gr. Sandusky | 3.1 c.c. N/10 HCl |
| 1.0 gr. " | 6.0 c.c. " " |

These are only a few of the numerous results taken on this line of work, but they will show the point that I wish to bring out. An alkalimetry test means nothing as the results were variable. I tried to remedy this variation of results by the use of barium carbonate, but this did not benefit it. Next I tried benzine, thinking that the action of air had some effect. This did not change

things may. From a study of what I could find on the subject of decomposition of cement by water by Le Chatelier[2], my results are what they should be. The results show that the cement goes into solution as fast as more water is added. Those compounds in the cement, that do not go into solution as such decompose, and the calcium oxide portion goes into solution. This referred to decomposition takes place very irregularly, and this alone, if it were not for the fact that the other compounds go into solution until the solution is saturated, would produce variations in the titration of the water extracts. I may as well state here that both from my own work, and from what I could find on the subject, that the test given for alkalimetry of water extract of cement by R. and W. Fresenius[1] does not mean anything and would not form the basis of a determination for calcium oxide.

(2) Study of the water extract of cement to see if it contains all the $SO_3$, that the cement contains.

With this end in view I took 1.0 gram of the cement, and treated it with 1000 c.c. freshly boiled water. I ran these results in duplicate. The end in view being to determine the percentage of the cement constituents extracted as $SO_3$.

[2] Jour. Soc. Chem. Ind. Vol. 3. 1884.

[1] Zeit. Anal. Chem. Vol. 23. page 175; Vol. 24, page 66; Vol. 32, page 448.

Results:--

1.0 gr. cement

1000 c.c. water

| | Sample #1. | | Sample #2. | |
|---|---|---|---|---|
| | Extract 100 c.c. | Extract 1000c.c | Extract 100 c.c | Extract 1000 c.c. |
| $SO_3$ weighed as $BaSO_4$ x .34352 Wt. | .0069 | .069 | .0072 | .072 |
| of $SO_3$. | .0023702 | .023702 | .002473 | .02473 |
| % cement extracted as $SO_3$ | 2.37 | | 2.473 | |

THE CEMENT PROPER ANALYSED FOR $SO_3$

Results:--

Taking 1.0 gr. of the cement.

| | Sample #1. | Sample #2. |
|---|---|---|
| $SO_3$ weighed as $BaSO_4$ | .0641 | .0636 |
| X .34352 = Wt. $SO_3$ | .0201 | .021447 |
| % $SO_3$ | 2.201 | 2.1447 |

These results show that all the $SO_3$ contained in the cement was extracted by water.

I verified this conclusion by an analysis of the cement residue not dissolved by the water and found that the residue did not contain any $SO_3$. I also analyzed a series of residues from other brands of cements and found that they did not contain any $SO_3$. Thus, I conclude that all the $SO_3$ contained in cement is

extracted by water.

(3) Study of water extract of cement after ten minutes contact with the water.

Treated 1.0 gr. of cement with 1000 c.c. of freshly boiled water. Took 100 c.c. of the water extract at the end of ten minutes, and evaporated to dryness after adding $H_2SO_4$ in excess.

| | Sample #1. | Sample #2. |
|---|---|---|
| Wt. of residue weighed as sulphate | .0325 gr. | .03[illegible] gr. |
| % of cement extracted weighed as sulphate | 32.5% | 32.3% |

I made these determinations as a check on results.

Now I analyzed these samples.

Results:--

| | Sample #1. | | | Sample #2. | | |
|---|---|---|---|---|---|---|
| | Extract 100 c.c | Extract 1000c.c | Extract Cement | Extract 100 c.c | Extract 1000c.c. | Extract Cement. |
| CaO | .010874 | .10874 | 10.874 | .0109 | .109 | 10.9 |
| MgO | .000579 | .00579 | .579 | .000506 | .00506 | .506 |
| $SiO_2$ | .0040 | .04000 | 4.000 | .0038 | .038 | 3.8 |
| $K_2SO_4$<br>$Na_2SO_4$ | .0007 | .007 | .7 | Lost. | | |
| Al | Trace? | | | Trace? | | |

These results calculated to sulphates checked up with the residues which had been previously weighed as sulphates. The results of this analysis calculated to all the possible forms in which these constituents are known to exist in cement, still leave an unsatisfied amount of calcium oxide. (Used $SO_3$ previously known to exist in my calculation.) This free lime may or may not exist as such in the original cement. Since it is known that the iron ferrite of calcium decomposes on treatment with water, it may be safely stated that not all if any of the calcium oxide unsatisfied existed as free lime in cement. My results verified the fact that the iron content of cement is not extracted by water. My work as far as this agrees with that of LeChatelier in his Edcomposition of Cement. This would afford a very extended study.

(4) The study of the Action of Ammonia Chloride on distillation with cement in the presence of water.

The work in detail is as follows:--Took 0.5 gr. of the cement, 1.0 gr. $NH_4Cl$, and 500 c.c. of water. This mixture was distilled down one half and the $NH_4OH$ given off collected in an N/3 HCl solution. The excess of the N/3 HCl sol. used was titrated back with N/3 $NH_4OH$ sol. using lacknoid as an indicator. I then calculated the N/3 HCl equivalent of the $NH_4OH$ given off to calcium oxide. Made some analyses of the ammonia chloride extracts. Determined the amount of the cement residue not extracted by the $NH_4Cl$ sol., and made some analyses of them.

Taken: 0.5 gr. Cement.

1.0 gr. $NH_4Cl$

500 c.c. Water

Results:--Calculated to per cent on .5 gr.

| Brands | $N/3$ HCl equivalent of $NH_4OH$ given off c.c. | $N/3$ HCl equivalent calculated to CaO % CaO | $NH_4Cl$ Extract Analysis. | | | | | | % Residue not extracted by $NH_4Cl$ | Residue Analysis. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | % $SiO_2$ | % $Al_2C_3$ + $Fe_2O_3$ | % MgO | % CaO | % $SO_3$ | % $Na_2SO_4$ $K_2SO_4$ | | % $SiO_2$ | % $Al_2O_3$ + $Fe_2O_3$ | % CaO |
| Sandusky (1) | 29.16 | 54.42 | 11.44 | 0.71 | 1.29 | 65.96 | 2.37 | 1.95 | 26.19 | 11.51 | 8.35 | 6.33 |
| Sandusky (2) | 29.16 | 54.42 | 11.08 | 0.69 | 1.19 | 55.91 | | | 25.90 | 11.59 | 8.47 | 6.29 |
| Dycherhoff (1) | 27.96 | 52.18 | 8.60 | 0.01 | 1.80 | 53.90 | 1.09 | 2.01 | 31.28 | 10.70 | 11.78 | 8.56 |
| Dycherhoff (2) | 28.01 | 52.25 | 10.03 | 0.02 | 1.50 | 53.36 | 1.10 | 1.85 | 31.32 | 10.90 | 11.59 | 8.48 |

After making a careful study of the results in the above table, I thought that the amount of $NH_4OH$ given off would be a means of determining the properties of the cement. With this end in view, I conducted the following experiments using the same method of treatment as that stated in the above analyses.

Taken:--0.5 gr. Cement.

1.0 gr. $NH_4Cl$ .

500 c.c. Water.

Results:--

| Brands. | N/3 HCl Equivl't of $NH_4OH$ given off | N/3 HCl Equivl't Calculated to CaO %CaO | % Residue not extr'd by $NH_4Cl$ | Residue Analyses: % $SiO_2$ | % $Al_2O_3$ $Fe_2O_3$ | % CaO |
|---|---|---|---|---|---|---|
| Alsen (1) | 28.94 | 54.00 | 31.3 | 15.7 | 8.65 | 6.7 |
| Alsen (2) | 28.79 | 53.72 | 31.5 | 15.5 | 8.85 | 6.72 |
| Chicago Portland (1) | 28.00 | 50.33 | 34.9 | 16.14 | 9.38 | 7.88 |
| Chicago Portland (2) | 28.06 | 50.4 | 34.8 | 16.02 | 8.2 | 7.89 |
| Hilton (1) | 27.28 | 50.9 | 35.2 | | | |
| Hilton (2) | 27.31 | 51.05 | 35.01 | | | |
| Buckeye | 29.62 | 55.2 | | | | |
| Atlas | 30.8 | 57.4 | 33.2 | | | |
| Alpha | 29.83 | 55.6 | | | | |
| Star Stettin | 28.77 | 53.7 | 32.4 | | | |
| NATURAL CEMENT | | | | | | |
| Utica (1) | 26.53 | 49.52 | 29.9 | 22.3 | 2.54 | 5.16 |
| Utica (2) | 26.54 | 49.50 | 30.0 | 21.9 | 2.59 | 5.29 |
| SLAG CEMENT. | | | | | | |
| Illinois Steel No. 1 | 16.37 | 35.5 | (This cement formed $NH_4S$ on distillation with $NH_4Cl$ instead of $NH_4OH$ as in case of other cements.) | | | |

Now I had a table prepared of the physical tests that were made on the above cements by the Civil Engineering department of the University of Illinois.

## TESTS OF PORTLAND CEMENTS.

| Brands | Weight per cubic foot | | Fineness, per cent passing sieve. | | | Activity interval elapsing between addition of water | | | | Tensile Strength 1 day in air. 6 days in water. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | No. of tests. | Pounds. | No. of tests. | 100 | 200 | Initial Set | | Final Set | | No. of tests | Pounds |
| | | | | | | Air h-m | Water h-m | Air h-m | Water h-m | | |
| Dycherhoff | 2 | 81.10 | 2 | 89.30 | 64.1 | | | | | 25 | 476 |
| Star Stettin | 2 | 78.60 | | | 75.6 | | | | | 10 | 485 |
| Hilton | 2 | 73.20 | 3 | 81.30 | 62.8 | 3-20 | 8-15 | 6-0 | | 16 | 509 |
| Chicago | 1 | 62.70 | 1 | 83.00 | 62.8 | 2-35 | | 4-10 | | 26 | 418 |
| Alpha | 2 | 82.70 | 2 | 88.40 | 67.5 | 4-0 | 8-30 | 9-30 | | 24 | 728 |
| Alsen | 1 | 67.60 | 2 | 87.50 | 64.6 | 1-10 | 19-0 | 1-28 | 24-0 | 11 | 638 |
| Buckeye | 1 | 66.30 | 1 | 83.40 | 60.4 | 3-0 | | 5-35 | | 13 | 183 |
| Atlas | 1 | 82.60 | 1 | 78.00 | 61.0 | | | | | 3 | 550 |
| Sandusky | 1 | 76.70 | 1 | 92.00 | 71.9 | 3-27 | 19-0 | 5-0 | 23-0 | 5 | 813 |

## NATURAL CEMENTS.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Clarke's Utica | 4 | 59.40 | 2 | 71.4 | 59.8 | 2-55 | 18-25 | 4-55 | 27-25 | 10 | 224 |

Compared the physical tests in the table with the results obtained by the action of $NH_4Cl$ and concluded that the more $NH_4OH$ set free from a cement by the $NH_4Cl$ did not always prove to be the best cement. This conclusion led me to think that the high results obtained for the $NH_4OH$ given off in the case of the weaker cements might be due to the presence of free lime. From the theory of the composition by Le Chatelier and S. B. and W. B. Newberry, reference No. 2&3, it is shown that the chief constituent of Portland Cement is tri-calcium silicate. Comparing this theory with my results it would seem that this compound sets free the $NH_4OH$. The next step was to try and determine the decomposition products of the tri-calcium silicate and see if they were present in the proper amounts, so as not to contain an excess of either the lime ($CaO$) or the $SiO_2$. With this end in view, the following work was carried out. Took 2.5 gr. cement, 5.0 gr. $NH_4Cl$ and 500 c.c. water. This mixture was boiled for 50 minutes, and the insoluble residue filtered off.

Taken:--2.5 gr. Cement.
5.0 gr. $NH_4Cl$.
500 c.c. Water.

Results:--

| Cement. | Silica in $NH_4Cl$ Extract. |
|---|---|
| Alsen | 1.24% |
| Hilton | 1.02% |
| Chicago Portland | 1.80% |

These results showed that the above conditions would not afford the retention of the $SiO_2$ from the decomposition of the tri-calcium silicate by the solution since the said $SiO_2$ of decomposition is 19.28%.

In order now to see if the amount of $NH_4OH$ given off would remain constant for a given cement, no matter what the quantity of cement taken, and to try and adjust the conditions so as to obtain all the silica of decomposition in the $NH_4Cl$ extract. I selected the Alsen cement as the one on which to solve the present problem. Took .25, 0.5 and 2.5 grs. of Alsen cement, 500c.c. of water, and 1.0 gr. of $NH_4Cl$, except in the case of the 2.5 gr. sample, where I took 5.0 grs. of $NH_4Cl$. Distilled down one half. Determined the N/3 HCl equivalent of the $NH_4OH$ given off, and calculated it to CaO. Determined also the $SiO_2$ in the $NH_4Cl$ extract.

Taken:--0.25, 0.5 and 2.5 grs. Alsen Cement.

1.0 gr. $NH_4Cl$ except in case of 2.5 grs., where

5.0 grs. $NH_4Cl$ were used.

500 c.c. Water.

Results:--

| Alsen Cement. | N/3 HCl equivalent of the $NH_4OH$ given off. | N/3 HCl equivalent calculated to CaO. % CaO. | $NH_4Cl$ Extract % $SiO_2$ |
|---|---|---|---|
| .25 grs. | 14.25 c.c. | 53.59 | 15.04 |
| .50 | 28.47 c.c. | 53.10 | 9.12 |
| 2.5 | 132.5 c.c. | 49.4 | 1.33 |

[illegible]

[illegible]

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| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
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| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

These results show that the $NH_4Cl$ equivalent of the $NH_4OH$ given off is proportional to the amount of cement taken, provided enough $NH_4Cl$ is taken to produce the decomposition in the presence of sufficient water. The % of $SiO_2$ in the three cases seem to hold a relation to each other. This relation seems to indicate a possibility of adjusting the conditions to such as will cause all the $SiO_2$ of decomposition to be retained by the $NH_4Cl$ extract solution.

With a view of studying the saturation ratio of the $SiO_2$ in the cement I conducted the following work. Took .125 and 25 grams Alsen cement boiled each down one half starting with 500 c.c. water and 2 grams $NH_4Cl$. Titrating the ammonia given off at the end of ten and fifteen minutes. Finally titrating when boiled down one half. Calculated all the N/3 HCl equivalent to calcium oxide. Determined the $SiO_2$ in the $NH_4Cl$ extracts. Extracted the cement residues with the 2% NaOH solution and determined the silica in this extract. Then I treated the residue not effected by the NaOH solution with HCl and determined the $SiO_2$, ($Al_2O_3$ $Fe_2O_3$) and CaO in the HCl extract.

Taken:--.125 grs. and .25 grs. Alsen Cement.

2.00 grs. $NH_4Cl$.

500 c.c. Water.

2% NaOH solution to extract residue not extracted

by the $NH_4Cl$ solution.

| | N/3 HCl titration of $NH_4OH$ given off at | | | N/3 HCl equivalent calculated to CaO % CaO | | | Total % $SiO_2$ in $NH_4Cl$ Extract | % $SiO_2$ in NaOH Extract | Analysis of HCl Extract | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 10 min c.c. | 15 min c.c. | End c.c | 10 min. % | 15 min. % | End. % | % | % | % $SiO_2$ | % $Al_2O_3$ $Fe_2O_3$ | % CaO |
| 0.125 grams | 6.0 | 0.55 | 0.068 | 45.2 | 4.1 | 0.50 | 13.18 | 1.17 | 3.60 | 7.30 | 6.85 |
| 0.250 grams | 11.42 | 1.72 | 1.06 | 42.6 | 6.4 | 3.92 | 5.10 | 6.70 | 1.39 | 6.72 | 6.58 |

The results indicate that the reaction between the cement and the $NH_4Cl$ takes place practically in about ten minutes, or more notably the reaction takes place at once under the proper conditions, but the $NH_4OH$ formed is retained by the solution. The analysis of the extracts do not lead to the desired end of the determining the $SiO_2$ of decomposition and it appears that the conditions are below the solubility ratio of the $SiO_2$ in the solution medium. Noting the effect of the NaOH solution in the above analysis, the method of treatment was changed as follows:--Took 0.5 grs. of Alsen Cement, distilled with 2.0 grs. of $NH_4Cl$ and 500 c.c. water. Titrated the $NH_4OH$ given off after 10, 20 and 30 minutes. Then, to the water, and residue in the flask, 5.0 grs. $K_2CO_3$ were added, and enough water to bring the solution bulk to the original 500 c.c. Distilled for 15 minutes, filtered hot, and determined the $SiO_2$ in the filtrate. Treated the insoluble residue with HCl and determined $SiO_2$, ($Al_2O_3$, $Fe_2O_3$) and CaO in the HCl extract.

Taken:--0.5 grs. Alsen Cement.
2.0 grs. $NH_4Cl$
500 c.c. Water
5.0 grs. $K_2CO_3$

Results:--

| | N/3 HCl titration of $NH_4OH$ given off at | | | N/3 HCl equivalent calculated to CaO % CaO | | | Total % CaO From 10, 20 and 30 minutes distillation | % $SiO_2$ in filtrate | Analysis of HCl Extract | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 10 min c.c. | 20 min. c.c. | 30 min c.c. | 10 min | 20 min | 30 min | | | % $SiO_2$ | % $Al_2O_3$ $Fe_2O_3$ | % CaO |
| 0.5 grams | 20.93 | 8.50 | 0 | 39.05 | 15.81 | 0 | 54.86 | 2.62 | 1.5 | 9.12 | 61.22 |
| 0.5 grams | 21.88 | 5.16 | 0.15 | 40.82 | 9.63 | 0.28 | 50.73 | 3.10 | 2.68 | 8.72 | |

From a study of the above results it is seen that $K_2CO_3$ decreases the $SiO_2$ solubility instead of increasing it. This and the

preceding attempt to adjust the conditions to those necessary to be able to get all the $SiO_2$ of decomposition in the $NH_4Cl$ extract has indicated that it can not be done, at least without the working with very small quantities of cement and large amounts of water. Not being able to succeed in getting the $SiO_2$ of decomposition from the tri-calcium silicate all in the $NH_4Cl$ extract, the attempt was made to get the oxide, that is, all of it, out of the extract. With this end in view, I performed the following experiments. Took one gr. of Alsen Cement, 100 c.c. water, and 2.0 grs. $NH_4Cl$, boiled thoroughly, and filtered off insoluble residue. Treated this insoluble residue with HCl (1 acid to 5 $H_2O$). Determined the residue after treatment with HCl and called it $SiO_2$. Analyzed the HCl extract for $SiO_2$, CaO and ($Al_2O_3$, $Fe_2O_3$). Finally I analyzed the $NH_4Cl$ extract for $SiO_2$ and CaO.

Taken:--1.0 gr. Alsen Cement.
100 c.c. Water.
2.0 grs. $NH_4Cl$.

Results:--

| Alsen Cement | % $SiO_2$ & CaO in $NH_4Cl$ ext. |  | % $SiO_2$ not extracted by HCl | Analyses of HCl extract. |  |  |
|---|---|---|---|---|---|---|
|  | $SiO_2$ | CaO |  | % $SiO_2$ | $Fe_2O_3$ $Al_2O_3$ | % CaO |
| 1.0 gram | 2.32 | 50.2 | 17.35 | 1.92 | 10.99 | 12.51 |
| 1 gram | 1.85 | 50.9 | 18.35 | 2.12 | 10.98 | 11.15 |

These results show that under the conditions by which they were obtained the decomposition was not entirely effected, since the amount of CaO calculated to be present in the $NH_4Cl$ extract from the $NH_4OH$ given off is 54%, while that found in the $NH_4Cl$ extract is 50.9%. This indicates that the amount of water present is an important condition necessary for effecting the complete decomposition.

In order to control the saturation ratio of $SiO_2$ in the $NH_4Cl$ extract, and at the same time produce a complete decomposition of the tri-calcium silicate, the conditions were changed as follows. Took 0.5 grs. Alsen Cement, 2.0 grs. $NH_4Cl$, and 200 c.c. water. Distilled and titrated the $NH_4OH$ given off at end of 15 and 20 minutes. Filtered and washed residue. Treated this residue with dil. HCl. Determined the residue not extracted by HCl ($SiO_2$). Analyzed the HCl extract for $SiO_2$, ($Al_2O_3$, $Fe_2O_3$) and CaO.

Taken:--0.5 grs. Alsen Cement.
2.0 grs. $NH_4Cl$.
200 c.c. Water.

Results:--

| Alsen Cement | N/3 HCl Titrat'n of $NH_4OH$ given off |  | N/3 HCl cal'ated to CaO %CaO |  | %$SiO_2$ not extracted by HCl | Analysis of HCl Extract |  |  |
|---|---|---|---|---|---|---|---|---|
|  | 10' | 20' | 10' | 20' |  | %$SiO_2$ | %$Al_2O_3$ $Fe_2O_3$ | %CaO |
|  | c.c. | c.c. |  |  |  |  |  |  |
| 0.5 grs. (1) | 24.8 | 1.6 | 46.3 | 2.98 | 18.4 | 1.6 | 9.1 | 6.6 |
| 0.5 grams (2) | 26.0 | .2. | 377 | .37 | 8.5 | Spoiled. |  |  |

General Conclusions of the Action of $NH_4Cl$ on Distillation with Cement in the Presence of Water.

(1) The amount of $NH_4OH$ produced by the action of $NH_4Cl$ on a cement is constant, and in proportion to the quantity of cement taken.

(2) The chief constituent of Portland Cement tri-calcium silicate, produces most all of the $NH_4OH$ given off.

(3) The iron and aluminium content of the cement are practically all insoluble in the $NH_4Cl$ solution.

(4) There is a calcium compound, or compounds insoluble in the $NH_4Cl$ solutions.

(5) The greater the amount of $NH_4OH$ given off by a cement on treatment with $NH_4Cl$ is not necessarily the better cement.

(6) In determination of the $SiO_2$ of decomposition of the tri-calcium silicate, I have not succeeded in controlling the conditions.

(7) I cannot see any relation between physical properties and the action of $NH_4Cl$ on cement thus far determined, but think that if the $SiO_2$ of the decomposition of tri-calcium silicate could be determine we would then be able to detect the presence of free lime, or an excess of $SiO_2$ in the cement. This end would enable the chemist in his mixing of the raw materials, to adjust them so as to have a finished product made up of the largest possible quantity of the cheap constituent, tri-calcium silicate.

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